Synthesis of Al2O3-ZrO2-TiO2-HAp Nano-ceramic Composites

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論 文 内 容 要 旨

Oxide ceramics show the excellent intrinsic properties such as the high biocompatibility, inertness, strong in compression, relatively low thermal expansion coefficient, an excellent wear resistance and corrosion resistance. But they have a limitation of application because of their inherent brittleness, low impact strength and low fracture toughness. In this work, I examined the synthesis of nano-sized oxide ceramic composites such as Al_2O_3-ZrO_2, Al_2O_3-ZrO_2(Y_2O_3), Al_2O_3-metal, ZrO_2-TiO_2 and ZrO_2-HAp-metal as well as their characterizations. Synthesized nano-sized oxide ceramic composites are attractive materials for application to structural materials, biomaterials and photocatalytic materials. In order to the improvement of their mechanical properties has been considered toughening mechanism by the microstructures control approach such as dispersion of appropriately selected nanoparticles, homogeneous nano coatings and the fabrication of nanocrystalline composites. The microstructural improvement like a nano grain size is expected to enhance the fracture strength. The author has proposed novel methods for synthesizing nano-sized ceramic composites using sol-gel, electroless deposition, impregnation, hot press, spark plasma sintering techniques.

Chapter 1 Introduction

In the first chapter, the author provides background of the present study on synthesis of oxide ceramic composite, their microstructure and properties with discussion of previous work. It includes gaps and the purpose of this research work, leading to brief description of the contents in this PhD thesis.

Chapter 2 Al_2O_3-ZrO_2 ceramic composite systems

This chapter deals with fabrication of Al_2O_3-ZrO_2 ceramic composites by sol-gel method, which enabled us to synthesize nano-sized Al_2O_3-ZrO_2 ceramic composites. According to the present work, two kinds of Al_2O_3-ZrO_2 ceramic composites: one is a typical 3-dimensional porous body having the pore size of 400~1000nm, the other is the sample material composite with a nanocrystalline phase (less than 20nm). In the case of porous Al_2O_3-ZrO_2

composite, the as-received composite powders are in an amorphous phase. By calcination of them at 900 °C, the c-ZrO_2 phase having 5nm average in diameter is crystallized. As the calcination temperature increases up to 1100 °C, a small amount of t-ZrO_2 phase is detected, although the main phase is c-ZrO_2. However, the Al_2O_3 particles in the Al_2O_3-ZrO_2 mixed powders exist in an amorphous phase up to 1100 °C. The porous Al_2O_3-ZrO_2 composite having ranged from 400-1000nm in pore size is successfully obtained using the Al_2O_3-ZrO_2 composite powders. The distribution of pores is homogeneous and it was closely related to the calcination temperature. The major phases of the porous composites are an m-ZrO_2 and α-Al_2O_3 although a t-ZrO_2 phase also is detected as a minor phase. The pore frames of the Al_2O_3-ZrO_2 composite are less than 400nm thick and they are made of nano crystalline with dense structure.

On the other hand, using the sol-gel Al_2O_3-ZrO_2(Y_2O_3) powder calcined at 400 °C, a typical nano-composite having a nano crystalline phase (less than 20nm) is successfully obtained by a pressureless-sintering process even at 1200 °C for 2hours. The values of relative density and Vickers hardness are comparatively high value with about 96.2% and 1100Hv, even though it is made at low temperature. The values are remarkably increased as the sintering temperature increases. In the composite sintered at 1400 °C, the hardness value is saturated with 1570Hv and the values of fracture toughness are almost same with about 6 MPa.m$^{1/2}$. The composite of Al_2O_3-ZrO_2 system give us excellent fracture toughness by using nano-particles of Al_2O_3/ZrO_2 as a starting sample before sintering. This leads to also reduce the sintering temperature close to HAp, enabling us to make composite of HAp-Al_2O_3/ZrO_2 system.

Chapter 3 Al_2O_3-metal systems

This chapter provides information on synthesis of Al_2O_3 matrix composite with metal powder dispersion by an electroless deposition process. After deposition, most of Al_2O_3 powders are coated with Ni layer having 20 nm thick, but some of nano-sized Ni particles also are attached on the Al_2O_3 powders. Microcracks and reaction compounds are not observed at the interfaces between the Al_2O_3 and Ni phases after pressureless sintering. The Al_2O_3-Ni composite is comprised of Al_2O_3, Ni and Ni_3P phases. A large number of dislocations are observed in the Ni phase due to the mismatch of thermal expansion coefficients between Al_2O_3 and Ni phases. The main fracture mode shows a mixed type with intergranular and transgranular modes having some roughness. The fracture toughness is increased due to the plastic deformation mechanism of the Ni phase in the Al_2O_3 matrix.

Nano-sized Ni-P coating layer having an amorphous structure is directly coated on the Al_2O_3 surface and the thickness of coating layer was about 5nm. Also, the nano-sized Ni-P particles having the particle size distribution from 5nm to 20nm are randomly adhered on the Al_2O_3 powders and exist between the Al_2O_3 powders. Hot pressed Al_2O_3-15wt% Ni-P composite shows excellent mechanical properties. The values of relative density, Vickers hardness and fracture toughness show high values of about 99.1%, 2360 Hv and 6MPa.m$^{1/2}$, respectively. The fracture toughness of Al_2O_3-Ni-P composite is improved by 2 times larger than that of α-Al_2O_3 pressureless sintered body, due to the plastic deformation mechanism of ductile phase like Ni-P. The main fracture mode shows the ductile fracture mode with intergranular type. From the results of micro-indentation test, the crack propagation is decreased by toughening mechanism combined of the crack branching and the crack deflection.

In the α-Al_2O_3 powders pretreated by the impregnation process, the Ag-coated Al_2O_3 composite powders with a core-shell structure are synthesized. The thin Ag layer on the α-Al_2O_3 powder is about 5 nm thick. Some nano-sized particles about 10nm in diameter also adhered to the α-Al_2O_3 powders. However, in the composite powder using

α-Al_2O_3 powders which were not pretreated, a core-shell structure is formed, but Ag particles with a size of about 100 nm in diameter are observed.

This composite material has unique mechanical properties due to the dispersion of metals such as Ni, Ni-P and Ag. The electroless deposition process enables us to coat metallic particles on the core particles with well dispersion. All the same, dispersion of nano Ag, Ni particles on the surface of Al_2O_3 particles gives us to improve mechanical properties of the composite. This is a challenging work to create a new microstructural control of ceramics.

Chapter 4 TiO_2-ZrO_2 composite systems

$TiO_2(1\text{-}x)\text{-}xZrO_2$ (x = 0.2, 0.4, 0.6 and 0.8) composite powders having a homogeneous distribution are successfully synthesized by sol-gel process. Synthesized TiO_2-ZrO_2 powders have a good homogeneity and amorphous TiO_2 particles adhere on the surface of 80nm t-ZrO_2 powders. The as-received TiO_2-ZrO_2 composite powders are strongly dependent on the calcination temperatures. In TiO_2-ZrO_2 composite powders calcined at 450 °C, TiO_2 is anatase type without dependency of contents. On the other hand, in the TiO_2-20wt%ZrO_2 composite powders calcined at 750 °C, anatase to rutile phase transformation is facilitated remarkably, while it was retarded in the TiO_2-80wt%ZrO_2 composite powders. The TiO_2-40wt%ZrO_2 and TiO_2-20wt%ZrO_2 composite powders calcined at 450 °C show an excellent photocatalytic activity, but in the sample calcined at 750 °C, the efficiency of methyl orange (MO) decomposition is reduced due to the appearance of rutile type. In the TiO_2-20wt%ZrO_2 composite powders, the TiO_2 particles consists of amorphous phase and it is crystallized into anatase after calcination at 600°C while they were changed to the rutile phase by further heating at 750 °C. In the case of TiO_2-20wt%ZrO_2 powders calcined at 600 °C, nano-sized TiO_2 particles having less than 30nm in diameter show the polycrystalline structure. At 750 °C, TiO_2 particles show a typical rutile TiO_2 phase having [111] zone axis. The particle sizes of TiO_2-ZrO_2 powders calcined at 600 °C are ranged from 10nm to 19nm. The photocatalytic activity of TiO_2-ZrO_2 powders for degradation of phenol showed that the composition of TiO_2-20wt%ZrO_2 is the most effective one. The photocatalytic activity increases with increased in TiO_2 content. The TiO_2-ZrO_2 composites show high photocatalytic activity at 350~550nm in wavelength.

Chapter 5 HAp-ZrO_2-metal systems

The nano-sized HAp coating layers are successfully achieved by plasma spraying. The thickness of HAp coating is in range of 100-150 μm, and no cracks are found at the interfaces between the HAp and ZrO_2 substrate. The heat treatment of as-sprayed HAp coating layer actually promotes the level of crystallinity, although the as-sprayed HAp coating layer exhibits a low degree of crystallinity. The Ca/P atomic ratio of the as-coated HAp layer and heat treated HAp coating is higher than that of the HAp powders. This may be due to the loss of P content in HAp powder during plasma spraying.

The HAp-Ag and HAp-ZrO_2 composites are fabricated by SPS process. The relative density of HAp sintered body can be enhanced by adding both Ag and ZrO_2 fine particles. The biaxial strength of the HAp-Ag composites decreases as Ag content increases. This may be caused by the existence of shrinkage cavities and pores due to the mismatch of the thermal expansion coefficients between HAp matrix and Ag particles during sintering process. The fracture toughness of HAp-Ag composite is slightly increased when Ag content of 5 vol% is added in the HAp matrix. The increase of fracture toughness is caused by the change of fracture mode.

The synthesis of HAp-10wt%Ag-20wt%ZrO_2 composite powders undergoes three continuous reactions: the synthesis of HAp by ultrasonic assisted synthesis method, the synthesis of Ag by electroless deposition process and the synthesis of ZrO_2 by sol-gel method. With regard to the as-received HAp-Ag-ZrO_2 composite powders, the HAp particles are appeared as a needle shape with 100nm in length and the Ag crystalline formed as a spherical shape with range from 10nm to 50nm in diameter, while ZrO_2 particles having 10nm in diameter exist in an amorphous phase. ZrO_2 in as-received powder is partially crystallized to c-ZrO_2 at around 450 °C. And also, the c-ZrO_2 crystalline is transformed to m-ZrO_2 at about 1208 °C. In the PLSed HAp-Ag-ZrO_2 composite, the major phase of ZrO_2 is m-ZrO_2 and small amount of c-ZrO_2 is detected. And then only one phase of β-TCP is detected without HAp phase due to the thermal decomposition of HAp phase. The concentration of Ag is remarkably decreased due to the melting of Ag. In the SPSed HAp-Ag-ZrO_2 composite, nano-sized Ag and ZrO_2 particle are homogeneously embedded in the HAp matrix. Its relative density and Vickers hardness are comparatively low value with about 95.0% and 350 Hv even then it is made by SPS process, while the fracture toughness show enhanced value of 2 times higher than that of SPSed HAp composite.

Chapter 6. Summary

This chapter summarized conclusions from the works described in the each chapter. The composite of Al_2O_3-ZrO_2 system give us excellent fracture toughness by using nano-particles of Al_2O_3/ZrO_2 as a starting sample before sintering. This leads to also reduce the sintering temperature close to HAp, enabling us to make composite of HAp-Al_2O_3/ZrO_2 system. All the same, dispersion of nano Ag, Ni particles on the surface of Al_2O_3 particles gives us to mprove mechanical properties of the composite. This is a challenging work to create a new microstructural control of ceramics. Addition of TiO_2 nano particles on the surface of ZrO_2 has been shown an excellent photocatalytic activity in the region of UV and visible wavelength. In addition to that, the retardation of phase transformation from anatase to rutile has been made by adding ZrO_2 into TiO_2 (A). This is very important finding and originality of this work due to usage of this composite at high temperature of around 1000 °C. SPS process gives us to present from the grain growth of HAp particles. This leads to improve the fracture behavior of the composite. The composite containing Ag has excellent antimicrobial characteristics.

論文審査結果の要旨

優れた特性を持つセラミックス素材を合成するには、原料組成の組み合わせの他に原料粒子の超微細化とその制御された分散が決め手になる。原料の超微粒子化は焼結温度の低下につながり、異種組成のセラミックスの組み合わせにおける成形体の焼結では、焼結温度の整合性が重要になる。また、セラミックスと金属とのサーメット材料でも、金属の融点とセラミックスの焼結温度とを近づける工夫が必要になる。しかしながら、複合セラミックス製造において、異種素材原料の微粒子化と焼結特性ならびに焼結体特性との関連性を系統的に調べた研究例は少ない。

本研究は、アルミナ(Al_2O_3)、ジルコニア(ZrO_2)、チタニア(TiO_2)ならびにヒドロキシアパタイト(HAp)の4種類の酸化物セラミックスとNi,Agなどの金属を選定し、これらを組み合わせて、構造材料、生体材料、光触媒のそれぞれの機能を発揮させ、その特性向上を目指す上での、異種原料の微粒子化やナノ構造化による気孔率制御、焼結温度の均衡化・低温化、光触媒特性の向上ならびに生体材料においては一定レベルの力学的特性を維持しつつ、抗菌性などを具備させる手法を開発した研究であり、全編6章よりなる。

第 1 章は緒論であり、複合化セラミックス合成法、焼結体の特性などに関する過去の研究を網羅し、その特徴を述べ、また、重要ながら未解明な事項を列挙し、その上で、本研究の目指す方向とその概要を述べている。

第 2 章は、$Al_2O_3-ZrO_2$系複合セラミックスに対し、その不活性バイオ材料としての破壊靭性向上は、Al_2O_3マトリックスの破壊靭性の劣勢を、ZrO_2超微粒子をマトリックス中に分散させることによって補完できるとする新しい複合酸化物合成法を提案した内容である。ZrO_2超微粒子のAl_2O_3マトリックス中への分散効果は、焼結温度の均衡化にも貢献するという重要な知見を得ている。

第3章は、Ni、Ni-PやAg超微粒子をAl_2O_3マトリックスに分散させ、構造材料としての破壊靭性向上の可能性を示唆した検討結果を纏めている。金属超微粒子はセラミックス相の破壊に伴いクラックの伝播に対しピン止め効果を果たすことをミクロ観察などで確認し、その複合体の力学的特性の向上に寄与するという知見を得ている。

第4章は、ZrO_2-TiO_2系セラミックス前駆体をゾルゲル法で調整し、焼成して光触媒となりうるTiO_2系複合セラミックス合成手法を提案し、合成物の光化学特性評価について検討した結果を述べている。特に、光触媒特性を最大にするZrO_2超微粒子のTiO_2相への分散割合が存在することを見出している。

第5章は、HAp-ZrO_2系、HAp-Ag系ならびにZrO_2-HAp-Ag系の活性バイオセラミックスをスパークプラズマ法で合成する手法を提案している。組織がナノサイズになるとZrO_2の焼結温度が低下し、HApの熱分解が抑制できること、かつ、セラミックスの機械的特性も優れることを示している。さらに、Agの抗菌性とHApの脆性についての検討も重要なデータを提示している。

第6章は結論であり、各章の結言を要約している。

以上、要するに本論文は、Al_2O_3-ZrO_2-TiO_2-HAp系の組み合わせによる複合セラミックスの製造において、異種素材原料のナノ微粒子分散による焼結特性ならびに焼結体特性を系統的に調べた研究であり、素材工学、物質科学の分野の発展に寄与するところ少なくない。

よって、本論文は博士(学術)論文として相応しく、合格と認める。